# Determination of Microamounts of Calcium, Magnesium and Aluminium in Titanium Metal

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**Synopsis**

As the complete separation of calcium, magnesium and aluminium from titanium metal is difficult, it was examined by extracting titanous thiocyanate with ether, and satisfactory results were obtained. Photometric determination was carried out after separation by using chlorophenol azodihydroxynaphthalenesulfonate for calcium, titan yellow for magnesium and extraction of the oxinate for aluminium.

## I. Introduction

Photometric determination of minute amounts of calcium, magnesium and aluminium contained in titanium metal requires complete separation of these elements without any loss from a large amount of titanium present.

In the determination of calcium, magnesium and aluminium, a process of removing titanium by extraction with cupferron and chloroform[1] is generally used, which is, however, time consuming and wasteful, when a large amount of the sample is taken. There are other methods of precipitating and separating magnesium alone with sodium hydroxide in the presence of hydrogen peroxide[2][3] or aluminium alone with ammonium hydroxide[4].

Patscheke and Schaler[5] separated a small amount of $Ti^{3+}$ by the extraction with ether in hydrochloric acidity or neutral solution, in the presence of potassium thiocyanate. In the present study, the separation of a majority of titanium was examined by applying this method, and photometric determination of calcium, magnesium and aluminium was also carried out by the usual colorimetric method, and satisfactory results could be obtained.

## II. Experimental method

### 1. Method of separation of titanium

Patscheke and Schaler carried out the separation of $Ti^{4+}$ from 0.05~0.1 g of $Ti^{3+}$ by extraction with ether in the presence of potassium thiocyanate. In order to see whether this method is applicable to the separation of a large amount of

* The 873rd report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals, **20** (1956), 212.

(1) J. A. Corbett, Analyst, **78** (1953), 20.
(2) J. M. Thompson, Anal. Chem., **25** (1953), 1231.
(3) Kitamura, Japan Analyst, **3** (1954), 254.
(4) Kitamura, Japan Analyst, **3** (1954), 329.
(5) Patscheke and Schaler, Z. anorg. allgem. Chem., **235** (1938), 266.

titanium, such as in titanium metal containing a minute amount of impurities, examinations were made as to the amount of potassium thiocyanate to be added, the kinds of acids used, the acid concentrations and the volume of the solution in the case of ether extraction.

( i ) Amount of potassium thiocyanate

To see the suitable amount of potassium thiocyanate required to transfer $Ti^{3+}$ present to ether layer as a thiocyanate complex, the following experiments were carried out with titanous chloride solution:

To 5 ml each of titanous chloride solution (10 g of titanium sponge dissolved by heating in 80 ml of hydrochloric acid and diluted to 100 ml with water) in a separatory funnel, various amounts of saturated potassium thiocyanate solution (1 g/ml) were added, the deposited salt was dissolved by adding small amount of water, and the solution was brought to 21 ml in total and adjusted to 2 N hydrochloric acid concentration. This solution was shaken with 50 ml of ether while cooling with running water, the aqueous layer was separated after standing, and the amount of titanium in this solution was determined, from which the amount of titanium extracted was calculated. The results are shown in Table 1.

Table 1. Effect of KSCN concentration on the Ti extraction.

| Ti taken (g) | KSCN added (g) | Ti remained in aq. layer (g) | Ti extracted in solvent (%) |
|---|---|---|---|
| 0.5 | 2 | 0.3633 | 27.34 |
| 0.5 | 3 | 0.2422 | 51.56 |
| 0.5 | 4 | 0.1083 | 78.34 |
| 0.5 | 5 | 0.0242 | 95.16 |
| 0.5 | 6 | 0.0132 | 97.36 |
| 0.5 | 7 | 0.0112 | 97.76 |
| 0.5 | 8 | 0.0156 | 96.88 |

HCl: 2 N, Ether: 50 ml, Total volume of aq. layer: 21 ml

As seen in this table, the extraction was good when over 5 g of potassium thiocyanate was added for each 0.5g of titanium.

(ii) Kind and concentration of the acid, and volume of solution for ether extraction

The effects of the kind and concentration of the acid used during extraction, and of the total volume of the solution on the extraction of titanium were examined in order to obtain optimal conditions.

To 5 ml (0.5 g Ti) each of the foregoing titanous chloride solution or titanous sulfate solution (10 g of titanium sponge dissolved by heating in 80 ml of sulfuric acid (1 : 3) and diluted to 100 ml), 6 ml (≒ 6 g) of saturated potassium thiocyanate solution was added, the precipitated salt was dissolved by adding small amount of water, and the solution was extracted with 50 ml of ether with various concentrations of the acid and various volumes of the solution. The amount of titanium in the aqueous layer was determined, from which the amount of titanium extracted was calculated, and the results are shown in Tables 2 and 3.

As shown in these tables, the extraction was good at around 2 N concentration of hydrochloric acid, and no great difference in the rate of extraction was given rise to small change in it. However, the extraction was effected better as the

Table 2. Effect of HCl concentration and total volume on the titanium extraction.

| HCl (N) | Total volume (ml) | Ti remained (g) | Extracting ratio (%) |
|---|---|---|---|
| 1 | 20<br>25<br>30 | Emulsion (separation was impossible) | |
| 1.5 | 20 | 0.0503* | 89.94* |
| | 25 | 0.0320 | 93.60 |
| | 25 | 0.0324* | 93.52* |
| | 30 | 0.0580 | 88.40 |
| 2.0 | 20 | 0.0143 | 97.14 |
| | 20 | 0.0184* | 96.32* |
| | 25 | 0.0280 | 94.40 |
| | 30 | 0.0649 | 87.02 |
| 2.5 | 20 | 0.0130 | 97.40 |
| | 20 | 0.0219* | 95.62* |
| | 25 | 0.0415 | 91.70 |
| | 30 | 0.0525 | 89.50 |
| 3.0 | 20 | 0.0490 | 90.20 |
| | 20 | 0.0393* | 92.14* |
| | 25 | 0.0490 | 90.20 |
| | 40 | 0.1050 | 79.00 |

Ti : 0.5 g, KSCN : 6 g, Ether : 50 ml, * : $NH_4SCN$ was used.

Table 3. Effect of concentration of $H_2SO_4$.

| $H_2SO_4$ (N) | Total volume (ml) | Ti remained (g) | Extracting ratio (%) |
|---|---|---|---|
| 1 | 25 | 0.1095 | 78.10 |
| 2 | 25 | 0.1175 | 76.50 |
| 3 | 25 | 0.1517 | 69.66 |
| 1 | 25 | 0.0553* | 88.94* |
| 2 | 25 | 0.0519* | 89.62* |
| 3 | 25 | 0.0648* | 87.04* |

Ti : 0.5 g, KSCN : 6 g, $NH_4SCN$ : 6 g, Ether : 50 ml, * : $NH_4SCN$ was used.

volume of the solution became smaller. In the case of hydrochloric acid, the use of ammonium thiocyanate in place of its potassium salt gave the same result, but the presence of ammonium salt interfered with the determination of calcium and magnesium and it is necessary to decompose it if present.

The rate of extraction was low when sulfuric acid was used, and in this case, the use of ammonium thiocyanate gave a somewhat better result than that of potassium thiocyanate.

It was concluded from these results that with 0.5 g of titanium, the addition of over 5 g of potassium thiocyanate, and the extraction carried out at around 2 N concentration of hydrochloric acid and in as small volume as possible would effect the extraction and separation of a majority of titanium by one procedure.

Table 4. Extraction of various amounts of Ti.

| Ti taken (g) | KSCN added (g) | Extraction (times) | Amounts of ether used (ml) | Extracting ratio (%) |
|---|---|---|---|---|
| 1 | 10 | 3 | 110 | 99.52 |
| 1 | 15 | 3 | 100 | 99.22 |
| 2 | 25 | 2 | 130 | 98.83 |
| 3 | 30 | 3 | 160 | 98.72 |

Table 4 shows the results obtained on the extraction of larger amounts of titanium. It was found that the majority of titanium present in about 3 g was removed by repeated extraction with ether after the addition of potassium thiocyanate little by little until the aqueous layer became colorless.

From the foregoing facts, it will be seen that this separation can satisfactorily be applied to the removal of titanium in titanium metal samples.

2. Effect of ether extraction on the determination of calcium, magnesium and aluminium

The following experiments were carried out to see whether the amount of calcium, magnesium and aluminium concurrently present would remain completely in the aqueous solution when titanium is separated by ether extraction.

Because of the unavailability of titanium metal containing known amounts of calcium, magnesium and aluminium, 20 g of high quality titanium sponge was dissolved by heating in 200 ml of hydrochloric acid and diluted to 500 ml with water to prepare the titanous chloride solution. To 25 ml (1 g Ti) of it, a definite amount of standard solution of calcium, magnesium or aluminium was added, and the solution was used as sample for the determination of calcium, magnesium or aluminium. 12 ml of saturated potassium thiocyanate solution was added to this solution, and the solution was brought to 42 ml in total and approximately 2 N concentration of hydrochloric acid. This was extracted three times with the total volume of 120 ml of ether to separate titanium. The aqueous layer was transferred to a beaker, ether was evaporated, and then the solution was oxidized with nitric acid. After the separation of a small amount of titanium and iron with ammonium chloride and ammonium hydroxide, calcium was precipitated as calcium oxalate, and determined by the potassium permanganate titration. After the removal of calcium, magnesium in the residual solution was determined by the gravimetric method with oxine in ammoniacal solution. Aluminium was determined by the gravimetric method with oxine from a portion of the solution that was poured into sodium hydroxide solution, from which titanium and iron were removed. At the same time, titanous chloride solution itself was treated in the same way

to determine the amount of calcium, magnesium and aluminium present in this solution. The values thereby obtained were subtracted from the foregoing determined values as blank values. The results are shown in Table 5.

Table 5. Influence of titanium extraction on the determination of Ca, Mg and Al.

| Ti taken (g) | Ca | | | Mg | | | Al | | |
|---|---|---|---|---|---|---|---|---|---|
| | Added (mg) | Found (mg) | Difference (mg) | Added (mg) | Found (mg) | Difference (mg) | Added (mg) | Found (mg) | Difference (mg) |
| 1 | 4.04 | 4.02 | −0.02 | 3.96 | 3.89 | −0.07 | 2.99 | 2.99 | 0.00 |
| 1 | 4.04 | 4.07 | +0.03 | 3.96 | 3.97 | +0.01 | 2.99 | 3.05 | +0.06 |
| 1 | 4.04 | 4.12 | +0.08 | 3.96 | 3.99 | +0.03 | 2.99 | 2.97 | −0.02 |

As shown in this table, calcium, magnesium and aluminium were found to remain almost completely in the aqueous solution after ether extraction.

From the foregoing results, it was confirmed that this method of separation was applicable to the determination of calcium, magnesium and aluminium in titanium, similar to the method of ether separation of iron utilized for the determination of trace elements in iron and steel samples.

3. Determination of calcium, magnesium and aluminium

In general, titanium metal contains minute amount of calcium, magnesium and aluminium, and these elements are hardly determined by the gravimetric or volumetric method. Therefore, photometric determination of these elements was examined from the solution obtained after removal of a majority of titanium. Determination of calcium was carried out with plasmocorinth B[6] (sodium chlorophenol-azo-dioxynaphthalene-disulfonate) often used for the microdetermination of calcium, magnesium with titan yellow[7], and aluminium with oxine-benzene extraction[8], followed by photometric determination with the Pulfrich's photometer. Titanium sponge was used as the sample, because a metal sample containing known amounts of calcium, magnesium and aluminium was unavailable.

A definite amount of a standard solution of calcium, magnesium or aluminium was added to the solution of 2 g of titanium dissolved by heating in 25 ml of hydrochloric acid. Such a solution was transferred to a separatory funnel, 20 ml of saturated potassium thiocyanate solution was added, and this mixture was diluted with water until the salt was dissolved completely. This solution was repeatedly extracted with ether to remove the most of titanium, the aqueous solution was transferred to a beaker, and ether was evaporated. Nitric acid was then added to this solution to oxidize titanous and ferrous and to decompose the excess of potassium thiocyanate. After cooled, the solution was transferred to 100 ml measuring flask, brought up to the mark with water, and used as the sample for determining calcium, magnesium or aluminium. 25 ml of this solution was

(6) Yanagisawa, Japan. Med. J., No. 1475 (1952), 2552.
(7) Sandell, *Colorimetric Metal Analysis*, 2nd Ed., 418.
(8) Kakita and Yokoyama, Japan Analyst, **2** (1953), 106.

taken and free acid was neutralized almost with sodium hydroxide, 3 g of sodium acetate was added, diluted with water, and boiled to precipitate titanium hydroxide and ferric hydroxide. After filtration, the precipitate was washed with hot water, the filtrate and washings were combined in a 100 ml measuring flask, and brought up to the mark. With each 15 ml of this solution, calcium and magnesium were determined photometrically by the Plasmocorinth B and titan yellow method, respectively. For the determination of aluminium, 25 ml of the original solution which titanium was extracted was poured into sodium hydroxide solution, titanium unextracted was coprecipitated with ferric hydroxide and the filtrate obtained was submitted to photometric determination by the oxine-benzene extraction.

At the same time, 2 g of titanium alone was treated in the same way, and the amounts of calcium, magnesium and aluminium contained in it were determined as the blank value. The results are shown respectively in Tables 6, 7 and 8.

Table 6. Determination of Ca in synthetic sample.

| Ti taken (g) | Blank (as Ca) (mg) | Ca added (mg) | Total Ca (mg) | Ca determined (mg) | Difference (mg) |
|---|---|---|---|---|---|
| 2 | 0.092<br>0.092<br>0.092 } 0.092 | 0.598 | 0.690 | 0.719<br>0.725<br>0.725 | +0.029<br>+0.035<br>+0.035 |

Ca was determined photometrically by using "Plasmocorinth B" reagent.

Table 7. Determination of Mg in synthetic sample.

| Ti taken (g) | Blank (as Mg) (mg) | Mg added (mg) | Total Mg (mg) | Mg determined (mg) | Difference (mg) |
|---|---|---|---|---|---|
| 2 | 0.937<br>0.950<br>0.952 } 0.946 | 0.750 | 1.696 | 1.725<br>1.700<br>1.713 | +0.029<br>+0.004<br>+0.017 |

Mg was determined photometrically by using "Titan yellow" reagent.

Table 8. Determination of Al in synthetic sample.

| Ti taken (g) | Blank (as Al) (mg) | Al added (mg) | Total Al (mg) | Al determined (mg) | Difference (mg) |
|---|---|---|---|---|---|
| 2 | 1.483<br>1.466<br>1.469 } 1.472 | 0.597 | 2.069 | 2.066<br>2.083<br>2.075 | −0.003<br>+0.014<br>+0.006 |

Al was determined photometrically by using "Oxine" reagent.

It was found from these results that the minute amount of calcium, magnesium and aluminium present in titanium could be determined by the methods described above, and accordingly, the following analytical procedures were adopted.

4. Analytical procedure

( i ) Removal of titanium

2 g of the sample is placed in a beaker, 25 ml of hydrochloric acid is added, and gently warmed to dissolve the sample. Insoluble residue, if any, is filtered, washed with 1 N hydrochloric acid, and the combined filtrate and washings are submitted to the next procedure. (The residue and the filter paper are ashed in a platinum crucible, fused with sodium carbonate, and digested with hydrochloric acid (1 : 4). This solution is combined with the aqueous layer separated from ether). After cooled, the solution is transferred to a separatory funnel (A), 20 ml (≒ KSCN 20 g) of saturated potassium thiocyanate solution is added and the salt formed is dissolved by the addition of as small amount of water as possible, while cooling with running water. This solution is shaken vigorously with 70~90 ml of ether for 1 minute under running water and the separated aqueous solution is transferred to another separatory funnel (B). In order to collect completely the water layer remaining in the pass of the cock of separatory funnel (A), 2~3 ml of hydrochloric acid (2 N) is added slowly along the wall and the water layer is transferred to the separatory funnel (B) after standing. To the solution in the separatory funnel (B), 1~2 ml of saturated potassium thiocyanate solution and 30~50 ml of ether are added, and this funnel is shaken while cooling under running water. This extraction with ether is repeated until the aqueous layer become only slightly yellow or colorless. (In general, suffice it to perform three times.) The aqueous layer is then transferred to a beaker, 10~15 ml of hydrochloric acid is added, and the solution is warmed gently to evaporate ether. Nitric acid is added drop by drop to this solution with caution to oxidize the small amount of potassium thiocyanate, titanous ion and ferrous ion remaining in the solution, and this solution is evaporated until the volume is reduced to 50~60 ml.

After cooled, this solution is transferred to a 100 ml measuring flask, brought to 100 ml with water, and this solution (A) is used for the determination of calcium, magnesium and aluminium.

(ii) Separation of calcium and magnesium

25 ml of this solution (A) is practically neutralized with 2 N sodium hydroxide solution, a few drops of saturated bromine water are added, and the whole volume is brought to 50 ml. This solution is boiled for a few minutes after the addition of 3 g of sodium acetate to precipitate titanium and iron. After allowing this to stand for some time, the mixture is filtered through a filter paper, the precipitate is washed with warm water, and the filtrate and washings are combined in a 100 ml measuring flask. This is diluted to 100 ml with water, shaken well, and used as the sample solution (B) for calcium and magnesium.

(iii) Determination of calcium

15 ml of the above sample solution (B) is placed in a 30 ml graduated test tube, and 2.5 ml of aqueous solution of plasmocorinth B (0.025 per cent) is added. While agitating this solution, 5 ml of 5 N sodium hydroxide solution is added and the whole volume is brought to 25 ml with water. After sufficient agitation, this

solution is allowed to stand for 5 minutes, transferred to a 10 mm cell, and its optical density at 610 mμ is measured with the Pulfrich's photometer. The amount of calcium is obtained from the calibration curve prepared at the same time. As the optical density of the solution varies with the concentration of the sodium hydroxide solution used and the developing color is somewhat unstable, the calibration curve for calcium should be prepared each time by preparing standard solutions with various known amounts of calcium, treated by the same procedures as for the sample solution, and the relation between the amount of calcium and its absorbancy is plotted which is used as a calibration curve. The absorbancy in this calibration curve decreased with increasing amount of calcium.

(iv) Determination of magnesium

15 ml of the sample solution (B) is placed in a 50 ml measuring flask, diluted with water to about 35 ml, and 1 ml of 5 per cent hydroxylamine hydrochloride solution, 1 ml of calcium chloride solution (1 per cent as calcium) and 1 ml of 0.15 per cent titan yellow solution are added. While agitating this mixture, 5 ml of 1 N sodium hydroxide solution is added to effect coloration. This solution is brought to 50 ml with water, shaken well and placed in a 30 mm cell. Its optical density at 530 mμ is measured with the Pulfrich's photometer, and the amount of magnesium is obtained from the calibration curve prepared beforehand.

The calibration curve for magnesium is obtained by using various known amounts of standard magnesium solution with the same procedure as the sample solution, that is, the relationship between the amount of magnesium and the absorbancy is plotted.

(v) Determination of aluminium

To 25 ml of the sample solution (A), 1 ml of 10 per cent ferric chloride solution is added and this is almost neutralized with 6 N sodium hydroxide solution. This solution is poured into 25 ml of hot solution of 20 per cent sodium hydroxide and the mixture is boiled for a few minutes. After cooled, this is transferred to a 100 ml measuring flask, diluted to the mark, shaken, and allowed to stand. This solution is filtered through a dry filter paper, the initial filtrate is discarded, and the subsequent 20 ml of the filtrate is pipetted out into a separatory funnel. 2 ml of 50 per cent ammonium nitrate solution and 3 ml of 3 per cent oxine acetate solution are added to this solution and the solution is adjusted to pH 8.6~9.2 with hydrochloric acid. To this solution, 15 ml of benzene is added through a burret, the mixture is shaken vigorously for 1 minute, and allowed to separate into two layers. The lower part of aqueous solution is discarded, the benzene solution is transferred to a 10 mm cell, and its optical density at 434 mμ is measured with the Pulfrich's photometer. The amount of aluminium is obtained from a calibration curve.

The calibration curve for aluminium is prepared by using a standard aluminium solution containing various known amounts of aluminium, which is treated by the same procedure as for the sample solution, and the relationship between the amount of aluminium and the absorbancy is plotted.

## III. Results

Results obtained on the determination of calcium, magnesium and aluminium in various kinds of titanium metal by the foregoing analytical procedures are shown in Table 9.

Table 9. Determination of Ca, Mg and Al in titanium sample.

| Sample | Ca (%) | Mg (%) | Al (%) |
|---|---|---|---|
| Ti (metal plate) | 0.013<br>0.013 | 0.490<br>0.487 | 0.072<br>0.069 |
| Ti (crude metal) | 0.055<br>0.054 | 0.030<br>0.031 | 0.073<br>0.075 |
| Ti (sintered) | 0.021<br>0.022 | 0.247<br>0.252 | 0.087<br>0.089 |


## Summary

Studies were made on the method for removing most of titanium by the extraction of titanous chloride with ether and the photometric determination of calcium, magnesium and aluminium in titanium metal.

(1) For the separation of titanium by ether extraction, the addition of over 5 g of potassium thiocyanate for every 0.5 g of titanium was neccessary, the concentration of hydrochloric acid for the extraction with ether should be about 2 N, and the volume of the solution to be extracted should be as small as possible for the efficient extraction.

(2) When sulfuric acid was used for dissolving the sample, the extraction was poor as compared with the use of hydrochloric acid, and the extraction of titanium with potassium thiocyanate was somewhat inferior to the use of ammonium thiocyanate.

(3) Examination of the loss of calcium, magnesium and aluminium during extraction with ether showed that these elements remained completely in the acid solution.

(4) Photometric determination of calcium by coloration with plasmocorinth B, that of magnesium with titan yellow, and that of aluminium by separation with sodium hydroxide and oxine-benzene extraction with its filtrate were all applicable to titanium samples.

(5) Analytical procedures for the determination of calcium, magnesium and aluminium in titanium metal was thereby established and their applications to actual samples gave satisfactory results.